solvent mixture of 50:50 methanol/water+1% acetic acid was used for all electrospray characterization experiments.

[0021] A stereo zoom microscope was used to monitor the electrospray in all the experiments and confirm spray stability. After the spray characterization, the microfabricated emitter array was further evaluated for its performance in electrospray ionization mass spectrometry, as shown in **FIG. 2***b*. A modified triple quadruple mass spectrometer (Sciex API 3000) was used in which the standard curtain gas-skimmer interface of the API 3000 was replaced with a heated multicapillary (7 _500 ím) inlet and an electrodynamic ion funnel interface for improved spray desolvation and ion transmission efficiency, as described in U.S. patent application Ser. No. 09/860,727 filed May 18, 2001, entitled "Improved Ionization Source Utilizing a Multi-Capillary Inlet and Method of Operation" by Smith et al. and U.S. Pat. No. 6,107,628 entitled "Method and apparatus for directing ions and other charged particles generated at near atmospheric pressures into a region under vacuum" also issued to Smith et al.

[0022] The spray emitter array was positioned ~5 mm away from the multicapillary inlet. The high-voltage dc power supply and syringe pump described in **FIG. 2***a* again provided electro-spray voltage and controlled liquid flow rate. Solutions of reserpine were used for evaluation of performance. The temperature of the heated multicapillary inlet was fixed at 200° C. A dc bias of 250 V was applied to the multicapillary block. The rf frequency and the amplitude applied to the ion funnel were 0.9 MHz and 130 Vp-p, respectively. The dc biases on the first ion funnel plate (25.4-mm i.d.) and the last ion funnel plate (2.3-mm i.d.) were 250 and 30 V, respectively, which resulted in an axial dc field of ~20 V/cm in the ion funnel. The mass spectrometer was operated in the positive ESI mode, and the selected ion monitoring (SIM) mode was used for the evaluation of sensitivity.

[0023] **FIG. 3** shows a photo of nine electrosprays generated from the nine-emitter array using the arrangement shown in **FIG. 1**. The emitter array was operated at a total infusion flow rate of 3 μL/min using a solvent mixture of 50:50 methanol/water +1% acetic acid. A stable electrospray was established from each emitter without the assistance of any nebulization gas, as demonstrated by the nine stable Taylor cones evident in **FIG. 3**. Interestingly, each electrospray showed a much smaller spray dispersion angle compared to that from a conventional single-capillary-plate configuration, which is ascribed to the significantly less divergent electric field between the electrospray emitter array and the counter plane electrode. The result is better focused electrosprays although a higher than typical voltage (~7 kV for the electrode separation of ~5 mm) is required to establish the stable electrosprays.

[0024] After stable electrosprays were established with the emitter array, the total spray ion current was measured at different liquid flow rates. To establish a baseline for all the comparisons, the total ion currents for single electrospray generated from both a conventional fused-silica capillary (100-im i.d. and 200-ím o.d. with the tip pulled down to 50 μm) and a microfabricated single-spray emitter were measured at different liquid flow rates. **FIG. 4** shows the total ion currents measured at different flow rates.

[0025] The fact that the two sets of data in **FIG. 4** correlate well indicates that the electrosprays had quite similar characteristics. It is also interesting to note from **FIG. 4** that the total electrospray current fits a 0.44 power of liquid flow rate, very close to the theoretical prediction of de la Mora and Loscertales as described in De la Mora, J. F.; Loscertales, I. G. *J Fluid Mech.* 1994, 260, 155-184. Their analysis concluded that, for electrosprays of highly conductive liquids, the dependence of the total electrospray current on the liquid flow rate could be formulated as,

$$I_s = f(\epsilon)(QKy/\epsilon)^{1/2} \quad (1)$$

[0026] where I_s is the total spray current from single electrospray, K is the electric conductivity of the liquid, y is the surface tension of the liquid, ϵ is the dielectric constant of the liquid, and Q is the liquid flow rate. Equation 1 was derived through a detailed dimensional analysis of the charge transport process through the Taylor cone and was verified by the authors experimentally using variety of liquid mixtures. Good agreement between the experimental results shown in **FIG. 4** and equation 1 supported the optical evaluation indicating that stable cone-jet mode electrosprays were obtained in the present studies.

[0027] Next, multielectrosprays were generated from the microfabricated chip using different numbers of emitters. The total ion currents of the multielectrosprays were measured at different liquid flow rates. The experimental data shown in **FIG. 5***a* clearly indicated that at each total liquid flow rate the total ion current increased as the number of the electrosprays increased. The results in **FIG. 5***a* also show that the total ion current from eight electrosprays was ~3 times higher than from a single electrospray at the same total liquid flow rate. The reason for this is evident from equation 1. If one assumes that each electrospray in the array behaves identically to a single electrospray, then from eq 1,

$$I^* = f(\epsilon)(Q^*Ky/\epsilon) \quad (2)$$

[0028] where I* and Q* are the ion current carried by each electrospray and the liquid flow rate supplied to each emitter in the array, respectively. It is apparent that Q* is smaller than the total liquid flow rate Q supplied to the emitter array. The total ion current of the multielectrosprays then becomes,

$$I_{Total} = \sum_{i=1}^{n} r_i$$

[0029] where n is the total number of electrosprays generated from the emitter array.

[0030] If we further assume that the liquid flow is distributed uniformly into every emitter, i.e., Q*) Q/n, each electrospray in the array will then carry the same ion current. Equation 3 becomes

$$I_{Total} = nI^* \quad (4)$$

[0031] Substituting eq 2 into eq 4, we have

$$I_{Total} = \sqrt{n} f(\epsilon)(Q^*Ky/\epsilon)^{1/2} = \sqrt{n} I_s \quad (4)$$

[0032] total ion current from the multielectrosprays, compared to the ion current from single electrospray at a given total flow rate, is proportional to the square root of the number of electrosprays. To verify equation 5, the experimental data shown in **FIG. 5***a* were normalized by the number of electrosprays in **FIG. 5***b*. All the experimental data collapsed to provide a good fit by a single curve. These